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Metal-Catalyzed Alkynylation of (Bromophenyl)oligophenylenes. A Rapid Route to
Thermoset Precursors of High Density Monolithic Glass-Like Carbon

by

E. B. Stephens and J. M. Tour

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Department of Chemistry and Biochemistry
University of South Carolina
Columbia, SC 29208

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Metal-Catalyzed Alkynylation of (Bromophenyl)oligophenylene.

Thermoset Precursors of High Density Monolithic Carbon Glass

Eric B. Stephens and James M. Tour*,¹
Department of Chemistry and Biochemistry
University of South Carolina
Columbia, South Carolina 29208

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The functionalization of (bromophenyl)oligophenylene with several alkynes is described. The bromide groups on the oligomer were replaced with terminal alkynes using a Pd/Cu catalysts system. Substitution of nearly all the original bromide locations was achieved. The functionalized oligomers, freely soluble in THF, exhibited high char yields on thermolysis to 900°C under a nitrogen atmosphere. Several of the functionalized oligomers flowed on heating. The oligomer that was functionalized with phenylacetylene exhibited a well-defined melting point at 190°C and acetylenic coupling did not take place until 310°C. The hot oligomer flowed to form a monolith of glassy carbon. Depending on the alkyne used, a range of densities from 1.39-1.95 g/cc could be obtained in the final carbon glass. The structure/property relationships and the material applications are discussed.

Carbon materials produced by the thermolysis of organic polymers have been used for numerous applications in, for example, the aerospace, electronic, medical implant and automotive industries.² Phenolic resins have dominated as thermoset precursors to carbon; however, phenolics typically exhibit 35-40% weight loss on thermolysis and densities of the char are ~1.3 g/cc.² Since phenolics exhibit large weight losses and low density chars, the use of multiple impregnation cycles (usually 6-7) are required for the production of high performance carbon products possessing densities of 1.8-1.9 g/cc.^{2,3} In an effort to limit the number of impregnation cycles (the cost-determining step) necessary for high density carbon preparation, the development of high char yielding materials from alkyne-containing organics has been investigated by many.⁴ Unfortunately, the difficulty in preparing the alkyne-containing monomers and the explosive nature of the multi-alkynylaromatics have retarded the rapid development and commercialization of this process.

We describe here the synthesis of oligomers possessing two required features that make them suitable for thermoset precursors to high performance, high density glassy carbon materials. First, the oligomers have very low weight loss (high char yield, low outgassing) on conversion to glassy carbon so that significant void volume will not result in the molds. Second, the materials exhibit a well-defined melting point, even a gravity-induced flowing, prior to conversion to carbon so that processing in the melt is possible to produce carbon monoliths.

We previously described a one step synthesis of brominated oligophenylenes from 1,4-dibromobenzene in dioxane with HMPA.^{5,6} Recently, we described an alternative procedure that does not require the use of the cancer suspect agent HMPA and affords a 65% yield of an ether insoluble portion of 1a ($n = m$) but possessing less *para* linkages than the oligomers prepared by the HMPA method (Figure 1).⁷

Figure 1

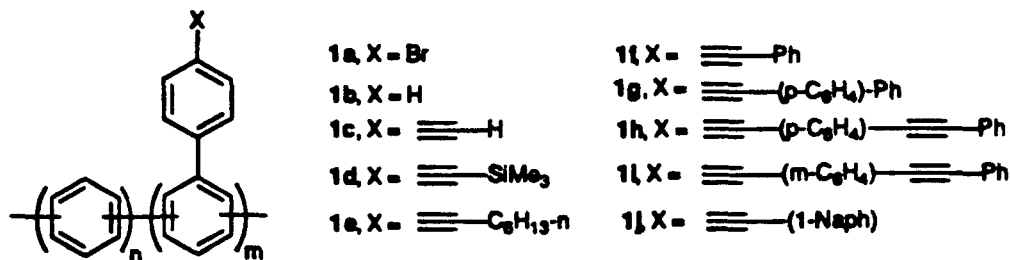


Table I

Compound	M_n^c	M_w/M_n^c	$T_{10\%}^d$	% Wgt Loss ^e	$T_g^{f,g}$	$T_m^{g,h}$	$T_{exo}^{g,i}$
1a ^a	500	3.9	400	48	---	155, 170	NA
1b	860	2.7	430	52	---	170, 225	NA
1c ^b	980	3.9	638	17.5	182	---	360
1d	570	6.6	378	27	---	140	160
1e	1010	3.3	430	33	---	140	170
1f	970	2.8	690	13.5	---	190	310
1g	1200	3.0	643	15.5	---	205	310
1h	1170	3.5	768	11.5	206	---	350
1i	1170	3.2	810	10.7	203	---	350
1j	1710	2.1	730	12.9	---	200	230

^aPrepared in THF without HMPA according to ref 7. All other compounds in this Table were prepared from 1a except 1e which was prepared from the brominated oligomer made with HMPA as in ref 5. ^bPrepared by treatment of 1d with K₂CO₃ in THF/CH₃OH. ^cDetermined by size exclusion chromatography (SEC) relative to polystyrene.⁹ ^dTemperature at which 10% weight loss occurred by thermogravimetric analysis (TGA) from ambient to 900°C at 20°C/min under an N₂ atmosphere. ^eTotal percent weight loss by TGA under the conditions listed in d. ^fOligomer glass transition temperature. ^gDetermined by differential scanning calorimetry (DSC) from 60°- 500°C at 20°C/min under an N₂ atmosphere. Dashed lines signify that these values were not clearly discernible by the DSC. ^hOligomer melt temperature. ⁱLarge exotherm characteristic of alkyne couplings. NA means not applicable.

All oligomers prepared were soluble in THF. Though 1a exhibits a high carbon to hydrogen (C/H) ratio, neither the brominated oligomer 1a nor the debrominated material 1b⁸ exhibited high char yields on heating (Table I).

In order to enhance the char yield, we needed to prevent volatilization on heating by appending a suitable thermo-activated cross-linking substituent. However, the moiety must not cross-link prior to the oligomer melting or else the desired flow properties would not be maintained. Additionally, the introduction of heteroatoms would be prohibited if a high char yield of carbon materials was to be achieved. Alkynes are known to form cross-linked alkenes and/or cyclotrimerize on thermolysis.⁴ Accordingly, we investigated the metal-catalyzed alkynylation of **1a** that would concomitantly replace the bromide heteroatoms. Following the Stephans-Castro/Sonogashira protocol,¹⁰ **1a** was treated with various terminal alkynes in a THF solution containing diisopropylamine, both a CuI catalysts and Cl₂Pd(PPh₃)₂ or Pd(PPh₃)₄ catalyst (23°C for 1 h, 60°C for 10 h, and 100°C for 5 h in a threaded screw cap reaction tube) to produce **1d-j**. In most cases, complete bromide substitution was achieved as determined by elemental analysis.¹¹

Several structure/property relationships were clearly evident and allowed us to rapidly converge on thermoset precursors for glassy carbon. Though **1c** exhibited a high char yield, the terminal alkyne was too unhindered and the cross-linking event occurred without a well-defined melt by DSC analysis. Oligomers **1d** and **1e** which have more hindered alkynes than **1c**, exhibited well-defined melts; however, the introduction of the aliphatic material decreased the C/H ratio resulting in a lower char yield than desired. Remarkably, by simply substituting **1a** with phenyl acetylene to produce **1f** (amorphous by powder x-ray diffraction (XRD)), we obtained a very high char yield and the oligomer exhibited a well-defined melt at 190°C while the coupling event did not occur until 310°C by DSC analysis. *Hence a 120°C processing window exists for this glassy carbon precursor.* Gravity flow of the melted material occurred to form a glossy black monolithic disc of glassy carbon. The polydispersity of **1f** could be lowered by purification of the oligomers by fractional precipitation; however, the flow properties then decreased significantly. Likewise,

when we phenylacetylated a brominated oligophenylene having more *para* linkages prepared by the HMPA route,⁵ the flow properties on thermolysis were impaired. Thus more rigid oligomer backbones are inferior. Compounds 1g-j were also prepared and studied; however, they offered no significant char yield advantage over 1f.¹² Moreover, the reagent necessary for 1f, phenylacetylene, is commercially available. The densities of the charred compounds also varied significantly. Carbon materials derived from 1f, 1h, and 1i, had densities of 1.83, 1.95, and 1.39 g/cc, respectively.¹³ This represents an unusually large range of structural variability obtainable in the carbon material. The very high densities and char yields of 1f and 1h make these materials attractive for use as thermoset precursors to high performance carbon materials by limiting the needed impregnation cycles to 1-2. Powder XRD of the charred material from the thermolysis of 1f, 1h, and 1i confirmed the presence of glassy carbon with no signals for the graphitic crystallite.

Hence, organometallic methods permit a two step (oligomerization and functionalization) entry into thermoset precursors for high density glassy carbon.

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Supplemental Material. Detailed experimental procedures for the preparation of the terminal alkynes and the preparation of 1a-j are provided as well as the TGA and DSC plots for 1a-j and the powder XRD plot of the char from 1f.

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(8) The debromination was achieved by treatment of 1a with *tert*-butyllithium as described in ref. 5 and 7.

(9) The SEC-determined M_w of these oligomers versus polystyrene standards was within 5% of the M_w values determined using oligophenylenes standards. See ref 5.

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(11) Less than 0.5% Br was detected by elemental analysis in 1e-j. Compounds 1c and 1d showed 3.00% and 5.85% Br, respectively.

(12) The thermolyzed compounds had the following appearances after the TGA analyses: 1a was a glossy black porous disc; 1b, 1d, 1e, and 1g each formed several glossy black droplets; 1c was a black powder; 1h and 1i each formed dull gray meshes; 1j formed a single glossy black droplet; and 1f formed a glossy black monolithic disc. Thus, in addition to 1f, compounds 1g, 1h, 1i and 1j appear to be suitable for glassy carbon thermosets if a typical hot pressure system is employed.

(13) The densities were calculated using the very finely ground charred materials suspended in halocarbon solvent mixtures of known density.